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DELIBERATE MODIFICATION OF THE BEHAVIOR OF N-TYPE CADMIUM TELLURIDE (U)

SEP 81 S TANAKA, J A BRUCE, M S WRIGHTON

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that depends on  $E_f$  of the redox couple in a manner consistent with a nearly ideal semiconductor. The reduced (dIe) exhibits an  $E_g$  of up to 0.9 V for a redox couple having  $E_f$  near 0.0 V vs SCE, whereas couples having  $E_f$  negative of -1.0 V vs SCE give zero photovoltage. Auger and X-ray photoelectron spectroscopy of the reduced and oxidized surfaces are qualitatively different. The reduced surface exhibits signals for Cd and Te in relative intensities that are consistent with a close to stoichiometric (1/1) surface. The oxidized surface exhibits little or no detectable Cd signal and the Te signal is consistent with a thick overlayer of elemental Te. The data are consistent with the conclusion that the (dIe/Te) interface is Fermi level pinned ( $E_f$  independent of contacting medium), the semimetallic Te overlayer behaves as a metal contacting (dIe and the (dIe/Te) interface energetics are therefore not influenced by changes in the contacting medium.

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TECHNICAL REPORT NO. 29

"DELIBERATE MODIFICATION OF THE BEHAVIOR  
OF N-TYPE CADMIUM TELLURIDE/ELECTROLYTE INTERFACES BY  
SURFACE ETCHING: REMOVAL OF FERMI LEVEL PINNING"

by

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Deliberate Modification of the Behavior of N-Type Cadmium Telluride/Electrolyte  
Interfaces by Surface Etching: Removal of Fermi Level Pinning

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Abstract: Single crystal, n-type CdTe ( $E_g = 1.4$  eV) has been studied with respect to barrier height,  $E_B$ , when contacting a liquid electrolyte solution containing a fast, one-electron, outer-sphere redox reagent. We approximate  $E_B$  as equal to the photovoltage measured by cyclic voltammetry of various redox couples at illuminated n-CdTe vs. a reversible electrode. N-CdTe surfaces pretreated with an oxidizing etch give an  $E_B$  of  $0.5 \text{ V} \pm 0.1 \text{ V}$  in  $\text{H}_2\text{O}/0.1 \text{ M NaClO}_4$  or  $\text{CH}_3\text{CN}/0.1 \text{ M} [\text{n-Bu}_4\text{N}]\text{ClO}_4$  that is independent of the  $E_0$  of the added redox couple. A reducing etch pretreatment gives an  $E_B$  in either of the electrolyte solutions that depends on  $E_0$  of the redox couple in a manner consistent with a nearly ideal semiconductor. The reduced CdTe exhibits an  $E_B$  of up to  $0.9 \text{ V}$  for a redox couple having  $E_0$  near  $0.0 \text{ V}$  vs. SCE, whereas couples having  $E_0$  negative of  $2-1.0 \text{ V}$  vs. SCE give zero photovoltage. Auger and X-ray photoelectron spectroscopy of the reduced and oxidized surfaces are qualitatively different. The reduced surface exhibits signals for Cd and Te in relative intensities that are consistent with a close to stoichiometric (1/1) surface. The oxidized surface exhibits little or no detectable Cd signal and the Te signal is consistent with a thick overlayer of elemental Te. The data are consistent with the conclusion that the CdTe/Te interface is Fermi level pinned ( $E_B$  independent of contacting medium); the semimetallic Te overlayer behaves as a metal contacting CdTe and the CdTe/Te interface energetics are therefore not influenced by changes in the contacting medium.

Results from this laboratory were recently reported<sup>2</sup> showing that n-type CdTe photoanodes give an open-circuit photovoltage,  $E_V$ , of  $\sim 0.5$  V independent of the electrochemical potential,  $E_{\text{redox}}$ , of the contacting electrolyte solution. Certain aspects of the results were independently reported.<sup>3</sup> A nearly constant barrier height,  $E_B$ , has been found<sup>4</sup> for n-CdTe contacted by metals having different work functions,  $\phi$ . The value of  $E_V$  is generally close to  $E_B$  at high illumination intensity. The finding of a constant  $E_B$  for n-CdTe, independent of  $E_{\text{redox}}$  or  $\phi$ , leads to the conclusion that n-CdTe is Fermi level pinned.<sup>2,5</sup>

We take the term "Fermi level pinned" to refer to a semiconductor that is measured to have a constant  $E_B$ , independent of the contacting medium for a wide range of  $E_{\text{redox}}$  or  $\phi$ . The origin of a constant  $E_B$  can be attributed to surface states situated between the top of the valence band,  $E_{VB}$ , and the bottom of the conduction band,  $E_{CB}$ . The density and distribution of surface states can control the value of  $E_B$  as a function of  $E_{\text{redox}}$  or  $\phi$ .<sup>5,6</sup> When the region between  $E_{CB}$  and  $E_{VB}$  is free of surface states,  $E_B$  of an n-type semiconductor is expected to vary with  $E_{\text{redox}}$  according to equation (1)<sup>7</sup> for  $E_{\text{redox}}$  situated between  $E_{VB}$  and  $E_{CB}$  where

$$E_V \approx E_B = |E_{\text{redox}} - E_{FB}| \quad (1)$$

$E_{FB}$  is the electrochemical potential of the semiconductor,  $E_f$ , when there is no band bending. When  $E_f = E_{FB}$  there is no accumulation or depletion of the majority charge carrier at the surface and  $E_B = 0$ . But even for surface-state-free semiconductors, equation (1) may not apply for all  $E_{\text{redox}}$  between  $E_{CB}$  and  $E_{VB}$ . It is possible that for  $E_{\text{redox}}$  sufficiently close to  $E_{VB}$  for an n-type semiconductor that the charge carrier distribution at the surface can be "inverted" giving more holes than electrons in the surface region. This results in a situation like that for a semiconductor

having surface states: additional positive movement of  $E_{\text{redox}}$  will not cause variation in  $E_g$ , rather additional potential drop across the interface will occur in the Helmholtz double layer in the electrolyte solution.<sup>8,9</sup>

For n-CdTe the origin of the constant  $E_g$  is most consistent with surface states rather than carrier inversion, since the range of  $E_{\text{redox}}$  where  $E_g$  is constant includes redox couples with  $E_h$  as negative as -2.0 V vs. SCE where carrier inversion would be very unlikely.<sup>2</sup> We use measured  $E_h$  values to approximate the formal potential of redox couples used in this study. When surface states are invoked it should be possible to manipulate the surface properties by surface chemical treatments.<sup>5,10,11</sup> Such treatments could include oxide formation, reversible adsorption of chemical species, covalent attachment of reagents, and other surface chemistry. We show in this paper that we can alter the behavior of n-CdTe from the Fermi level pinned situation to one where nearly ideal behavior, equation (1), is found by using a different surface pretreatment than used in the earlier studies of n-CdTe.



### Experimental Section

CdTe and Electrode Fabrication. Oriented single crystals of n-CdTe, (111) plane exposed,  $0.2 - 30 \Omega \text{ cm}$ , were obtained from Cleveland Crystals, Inc., Cleveland, Ohio. The crystals were polished first with  $20 \mu\text{m}$  alumina and then with  $10 \mu\text{m}$  alumina on a polishing glass. The crystals were finished with  $0.3 \mu\text{m}$  alumina on a polishing cloth (Politex Supreme PS, Gros Corp., Stamford, CT), fixed onto the glass. Ohmic contact was made to the CdTe by rubbing Ga-In eutectic onto the back of the crystal. A Cu wire was attached using conducting Ag epoxy. The Cu wire was encased in a 4 mm Pyrex tube and all surfaces but the exposed front surface of CdTe were sealed with ordinary epoxy. The exposed surface of the CdTe was the (111) face. Just prior to use all electrodes were etched and cleaned as described below.

Etching Procedures. Two different types of etchants were used, oxidizing and reducing. An oxidizing etch was one of the following: (i) 4 g  $\text{K}_2\text{Cr}_2\text{O}_7$ , 10 ml concentrated  $\text{HNO}_3$ , and 20 ml  $\text{H}_2\text{O}$ ; <sup>12</sup> (ii) 1/1/1 by volume saturated solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , concentrated  $\text{HCl}$ , and concentrated  $\text{HNO}_3$ ; <sup>13</sup> (iii) 3/2/1 by volume solution of 48%  $\text{HF}$ , 30%  $\text{H}_2\text{O}_2$ , and  $\text{H}_2\text{O}$  and then briefly rinsed with concentrated  $\text{HCl}$ ; <sup>14</sup> (iv) 3/2/1/0.01 by volume of concentrated  $\text{HNO}_3$ , concentrated  $\text{H}_2\text{SO}_4$ , glacial acetic acid, and concentrated  $\text{HCl}$ ; (v) 2/1/1 by volume solution of 48%  $\text{HF}$ , concentrated  $\text{HNO}_3$ , and glacial acetic acid. <sup>15</sup> For an oxidizing etch the CdTe electrode was immersed in the etchant for 30 s at  $25^\circ\text{C}$ . After etching the electrode was rinsed liberally with distilled  $\text{H}_2\text{O}$ .

For a reducing etch the electrode was first etched with oxidizing etchant (i) above for 30 s, rinsed with distilled  $\text{H}_2\text{O}$  and then immersed into a boiling solution of 2.5 M  $\text{NaOH}$  and 0.6 M  $\text{Na}_2\text{S}_2\text{O}_4$  for 3 min. The electrode was then rinsed liberally with distilled  $\text{H}_2\text{O}$ .

Chemicals. Spectrograde  $\text{CH}_3\text{CN}$  was freshly distilled from  $\text{P}_2\text{O}_5$  prior to use.  $[\text{n-Bu}_4\text{N}]\text{ClO}_4$  from Southwestern Analytical Chemicals was vacuum dried at  $70^\circ\text{C}$  for 24 h prior to use, and  $\text{NaClO}_4$  was obtained from commercial sources and used without further purification. Triply distilled  $\text{H}_2\text{O}$  was used for solvent in aqueous electrolyte systems.

Redox reagents were generally obtained from commercial sources; TMPD was purified by sublimation;  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ ,  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ ,  $\text{EuCl}_3$ , and 9,10-anthraquinone-2- $\text{SO}_3^-$  were used as received. Other redox couples are those used and purified in this laboratory previously.<sup>2,16</sup> Abbreviations for redox couples are  $\text{MV}^{2+} \equiv \text{N,N'-dimethyl-4,4'-bipyridinium}$ ;  $\text{TQ}^{2+} \equiv \text{N,N'-trimethylene-2,2'-bipyridinium}$ ;  $\text{TMPD} \equiv \text{N,N,N',N'-tetramethyl-p-phenylenediamine}$ ; and  $\text{AQ} \equiv 9,10\text{-anthraquinone-2-SO}_3^-$ . The  $E_{1/2}$  values are from cyclic voltammograms at Pt or Hg electrodes. The  $E_{1/2}$  value was taken to be the average position of the anodic and cathodic peaks.

Electrochemical Equipment and General Procedures. Electrolyte solutions were generally  $\text{H}_2\text{O}/0.1 \text{ M } \text{NaClO}_4$  or  $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$ . The non-aqueous electrolyte solution was passed through anhydrous neutral  $\text{Al}_2\text{O}_3$  just prior to use to insure dryness. In the case of  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  the supporting electrolyte was  $0.1 \text{ M } \text{KCl}$  because  $\text{Ru}(\text{NH}_3)_6^{3+}$  is not sufficiently soluble in  $0.1 \text{ M } \text{NaClO}_4$ . AQ in aqueous solution was studied in  $\text{H}_2\text{O}$  buffered to  $\text{pH} = 8.6$  using borax/ $\text{HCl}$ . All electrochemistry was carried out under a positive pressure of pure Ar.

Cyclic voltammograms were obtained using a PAR model 173 potentiostat driven by a PAR model 175 programmer. Data were recorded on a Houston Instruments X-Y recorder. The electrochemical cell was a single compartment cell consisting of a working electrode of n-CdTe, Pt, or Hg, a Pt counterelectrode, and a reference electrode. For aqueous electrolytes the saturated calomel reference electrode (SCE) was used. A  $0.1 \text{ M } \text{AgNO}_3/\text{Ag}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4/\text{CH}_3\text{CN}$  reference (+0.35 V vs. SCE) was used in  $\text{CH}_3\text{CN}$  solutions. All  $E_g$  determinations are from cyclic voltammograms at 100 mV/s.

For cyclic voltammograms redox reagents were added to solution at ~1 mM concentration in all cases. The n-CdTe electrodes were illuminated using a beam expanded He-Ne laser from Coherent Radiation, providing ~50 mW/cm<sup>2</sup> at 632.8 nm. This is sufficient light intensity to insure that photocurrent for ~1 mM solutions of redox reagent is limited by diffusion, not excitation rate (light intensity).

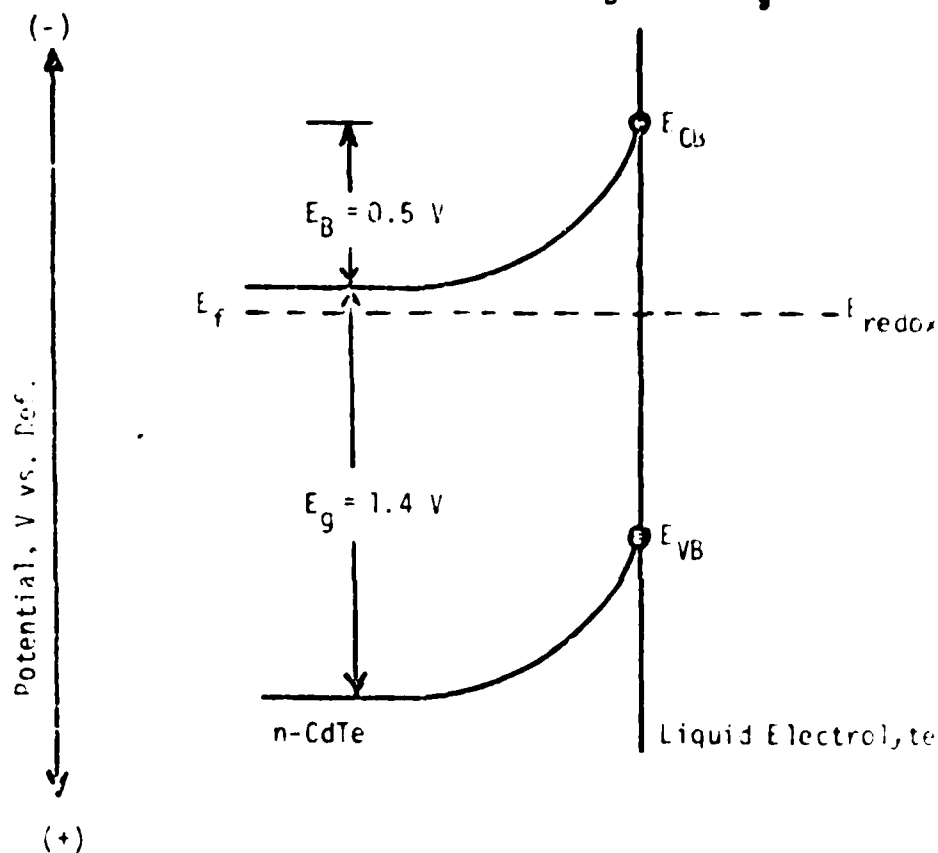
XPS and Auger Studies. Auger spectra were obtained on a Physical Electronics model 590A scanning Auger spectrophotometer. A 5 KeV electron beam with a beam current of 0.6 to 1  $\mu$ A was used as the excitation source. The samples were mounted by attaching the Cu wire lead to the sample holder to insure electrical grounding. A Physical Electronics model 04-303 differential ion gun was used to produce a 2 keV Ar<sup>+</sup> ion beam for sputtering. The pressure was maintained at  $\sim 3 \times 10^{-8}$  torr in the main vacuum chamber and  $1.5 \times 10^{-4}$  torr of Ar in the ionization chamber, while sputtering.

X-ray photoelectron spectra (XPS) were obtained on a Physical Electronics model 548 spectrometer with a magnesium anode. The broad scans (0-1000 eV) were recorded with a pass energy of 100 eV and the narrow scans with a pass energy of 25 eV. The peak energies at the Cd and Te peaks were referenced to the C 1s binding energy (284.6 eV) to correct for charging. Samples were mounted as above and sputtering was done with a 5 keV Ar<sup>+</sup> beam, after introducing Ar into the vacuum chamber to bring the pressure to  $\sim 7 \times 10^{-5}$  torr.

Elements detected by Auger and XPS were identified by reference to data previously reported using these techniques.<sup>17,18</sup>

## Results

a. Determination of  $E_g$  vs.  $E_{\text{redox}}$  for n-CdTe. Scheme I illustrates the interface energetics for n-type CdTe in equilibrium with a redox couple in an electrolyte solution where  $E_B = 0.5$ ;  $E_g$  is the band gap for CdTe, 1.4 eV.



Scheme I. Representation of n-CdTe/liquid electrolyte interface energetics when the barrier height,  $E_B$ , is 0.5 V.

In the previous studies,<sup>2,3</sup> the value of  $E_B$  was determined for  $\text{CH}_3\text{CN}$  electrolyte solutions and for CdTe etched with an oxidizing etch. We have extended these studies to aqueous solution and to CdTe etched with a reducing etch. The important finding is that the reducing etch results in an  $E_B$  that depends strongly on  $E_{\text{redox}}$  whereas the oxidizing etch gives an  $E_B$  that is independent of  $E_{\text{redox}}$  in either  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{CN}$ . We now detail the procedure used to determine  $E_B$  vs.  $E_{\text{redox}}$  and the data that have been collected in  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$  for "oxidized" surfaces and "reduced" surfaces of n-CdTe.

# 1. Procedure for Determining $E_B$ and the Classification of Redox Couples

Referring to Scheme I and equation (1), the maximum photovoltage,  $E_V$ , from the photoanode is equal to  $E_B$ . That is, when the  $E_f = E_{FB}$  the bands are no longer bent and  $E_f$  is  $E_B$  away from  $E_{redox}$ . We<sup>2,16</sup> and others<sup>9,19</sup> have used cyclic voltammetry of redox reagents at low concentration to measure  $E_B$  conveniently and rapidly for a wide range of redox couples. Generally, we choose fast, one-electron, outer-sphere redox reagents to avoid complications from adsorption, such as  $S^{2-}$  on  $CdS$ <sup>20</sup> or  $I^-$  on  $MoSe_2$ <sup>21</sup> and to insure that the energetics, not kinetics, dominate the measurement of the  $E_B$ . The procedure involves comparing the position of the peak of the photoanodic current,  $E_{PA}$ , in a cyclic voltammogram for the illuminated anode relative to the anodic current peak at a reversible electrode, e.g. Pt, for the redox couple under consideration. The anodic current peak gives the approximate electrode potential,  $E_f$ , where there is a 1/1 ratio of oxidized and reduced forms of the redox couple. The extent to which the peak at illuminated electrodes is more negative than at the reversible electrode is the photovoltage,  $E_V$ . And for sufficiently high light intensity this approximates the maximum open-circuit voltage possible. Thus, we take equation (2) to give the value of  $E_B$  within 100 mV.

$$E_B \approx E_V = |E_{PA,Pt} - E_{PA,n-Cd \text{ illum.}}| \quad (2)$$

At the very least, the procedure gives excellent relative values of  $E_V$  vs.  $E_{1/2}$  values for the redox couples when the reduced form is added at the same concentration and the light intensity is the same.

Depending on the observed behavior of the redox couple at the semiconductor, we class the redox couples into one of five classes according to the following criteria:<sup>16a</sup>

Class I -  $E_1$  is sufficiently negative that reversible behavior is observed at the semiconductor;  $E_1$  is more negative than  $E_{CB}$  and there is no photoeffect.

Class II-  $E_1$  is near  $E_{CB}$  but slightly positive of it so that dark oxidation is observed but rate is poor and is improved by irradiation with a small negative shift of the anodic current peak.

Class III- no dark oxidation of the reduced form of the couple;  $E_B$  depends on  $E_{redox}$  such that  $E_B$  is proportional to  $E_1 - E_{FB}$  for  $E_1$  between  $E_{FB}$  and  $E_{VB}$ .

Class IV- no dark oxidation of the reduced form of the couple but  $E_B$  independent of  $E_1$ .

Class V - redox couples having  $E_1$  sufficiently negative or positive that decomposition current for electrode is too great to allow study of the redox couple.

2.  $E_B$  in  $CH_3CN$  and  $H_2O$  vs.  $E_{redox}$  for Oxidized CdTe. Figure 1 and

Table 1 summarize  $E_B$  determinations for a number of redox couples in  $H_2O$  and in  $CH_3CN$  for n-CdTe that was etched using an oxidizing etch.

Generally, the oxidizing etches (i), (ii), or (iv) (see Experimental) give a value of  $E_B$  that is roughly independent of  $E_1$  for the redox couples used.

The data in Figure 1 and Table 1 for  $CH_3CN$  solution are from the previous work in this laboratory<sup>2</sup> and results for other oxidizing etches accord

well with these data. The data for  $H_2O$  solutions represent new

information and illustrate that  $E_B$  is essentially independent of  $E_1$  for a wide range of  $E_1$ 's. Study of redox couples in  $H_2O$  with  $E_1$  more

positive than +0.3 or more negative than -1.4 V vs. SCE is precluded by photoanodic or cathodic decomposition currents, respectively. In  $CH_3CN$  the range

is somewhat greater, consistent with the fact that it is well known that solvent can profoundly change the energetics for anodic and cathodic

decomposition processes.<sup>22</sup> Except for the Class V couples, all of the redox couples studied at n-CdTe treated with the oxidizing etch belong to Class IV.

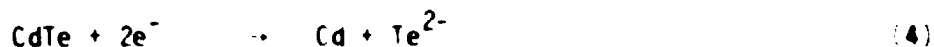
As reported previously,<sup>2,3</sup> the n-CdTe surface is not durable and the data given in Table I are for freshly etched surfaces for the first one to three cyclic voltammograms (100 mV/s) for a given redox couple. The positive potential limit was generally no further than 100 mV beyond the photoanodic current peak. Nonetheless, the photoanodic decomposition is a serious contributor to error and the values in Table I and Figure 1 represent the average of results of a number of determinations. The cyclic voltammetry of 1 mM  $\text{Fe(CN)}_6^{4-}$  in  $\text{H}_2\text{O}/0.1 \text{ M NaClO}_4$  is illustrative of the quality of the data, Figure 2. The  $\text{Fe(CN)}_6^{3-/4-}$  couple is durable and fairly reversible in  $\text{H}_2\text{O}$  at Pt, but the oxidation of  $\text{Fe(CN)}_6^{4-}$  is blocked in the dark at n-CdTe. Upon illumination of the n-CdTe with  $\geq E_g$  light  $\text{Fe(CN)}_6^{4-}$  is oxidized and the  $\text{Fe(CN)}_6^{4-} \rightarrow \text{Fe(CN)}_6^{3-}$  current peak is ~0.6 V more negative than at Pt. Note the large amount of photoanodic current just beyond the peak for the  $\text{Fe(CN)}_6^{4-} \rightarrow \text{Fe(CN)}_6^{3-}$ ; this current is attributable to the decomposition represented by equation (3).<sup>23a,b</sup>



Such decomposition can likely lead to sufficiently thick layers of elemental Te that the surface properties are significantly altered, vide infra. The main point is that the data regarding  $E_g$  need to be obtained within one to three cyclic voltammetry scans after etching to insure that the data reflect the properties of the freshly etched surface. At the deliberately low redox reagent concentrations needed to obtain mass transport limited oxidation currents there is simply not enough reducing agent to completely suppress the photoanodic decomposition. In order to exploit the n-CdTe in sustained photoelectrochemical energy conversion applications high concentrations of the redox reagent would be employed.

3.  $E_B$  in  $CH_3CN$  and  $H_2O$  vs.  $E_{redox}$  for Reduced CdTe. Figure 1 and Table II summarize the  $E_B$  determinations for n-CdTe that has been treated using the reducing etch. There is a remarkable difference in the set of data for the reduced CdTe vs. the oxidized CdTe. For reduced n-CdTe, unlike oxidized n-CdTe, the  $E_B$  depends on the  $E_y$  of the contacting redox couple. The dependence is nearly that expected for an ideal semiconductor, equation (1), where  $E_{FB} \approx -1.0$  V vs. SCE + 0.1 V in  $CH_3CN$  or in  $H_2O$ , in accord with an  $E_{FB}$  value determined from capacitance measurements in  $CH_3CN$ .<sup>3</sup> Importantly, the CdTe that has been treated with the reducing etch is essentially a reversible electrode in the dark for sufficiently negative redox couples unlike CdTe that has been treated with the oxidizing etch. No available redox couple is reversible in the dark at n-CdTe that has been etched with the oxidizing etch.

Figure 3 shows the cyclic voltammetry for the  $TQ^{2+}/+$  and  $TQ^{+}/0$  couples in  $CH_3CN/0.1$  M  $[n-Bu_4N]ClO_4$  for the reduced CdTe surface. The more positive  $TQ^{2+}/+$  wave is shifted negative (relative to the position at Pt) at the illuminated CdTe to a larger extent than is the  $TQ^{+}/0$  wave. For an oxidized CdTe each wave is shifted negative by 0.5 V relative to their positions at Pt. The small shift for the  $TQ^{+}/0$  wave is consistent with the fact that the  $E_y(TQ^{+}/0)$  is close to  $E_{FB} \approx -1.0$  V vs. SCE. Couples having  $E_y$  more negative than -1.0 V vs. SCE can be in Class I at the reduced CdTe but cathodic decomposition, equation (4) limits the negative range that can



be examined, vide infra. Couples such as  $TQ^{2+}/+$  and  $TQ^{+}/0$  where  $E_B$  varies with  $E_y$  are in Class III. All redox couples in the region positive of -0.9 V appear to belong to Class III but the positive limit to the range of  $E_y$ 's that can be tested is again determined by the potential onset for photoanodic decomposition, equation (3).



Figure 4 illustrates the difficulty that results from the competing photoanodic decomposition. A freshly etched (reduced) n-CdTe photoelectrode exhibits a photoanodic current peak for  $\text{Fe}(\text{n}^5\text{-C}_5\text{H}_5)_2 \rightarrow \text{Fe}(\text{n}^5\text{-C}_5\text{H}_5)_2^+$  at  $-0.3$  V vs. SCE and when the scan is not extended too far beyond the peak the scan is fairly reproducible. However, when the first scan is extended to a positive limit of  $+0.6$  V vs. SCE, the second scan reveals a photoanodic current peak that is shifted  $0.3$  V more positive. Apparently, the photoanodic decomposition current results in surface chemistry that alters the value of  $E_B$ . Interestingly, it appears that the photoanodic decomposition of the reduced n-CdTe results in a surface that gives a value of  $E_B$  that is similar to that for the oxidized n-CdTe from the oxidizing etch. In fact, it appears that the  $E_B$  that can be obtained for reduced n-CdTe using the  $\text{TMPD}^{2+}/+$  couple is controlled by the photoanodic decomposition that occurs, since the  $E_1(\text{TMPD}^{2+}/+)$  is so positive. When scanning the reduced n-CdTe in a  $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4/\text{TMPD}$  solution the  $E_B$  with respect to the  $\text{TMPD}^{+}/0$  couple is larger than with respect to the  $\text{TMPD}^{2+}/+$  couple on the first scan, but on the second scan the  $E_B$  is found to be the same, within  $100$  mV, for the two couples, Figure 5. Accordingly, the two most positive redox couples used in  $\text{CH}_3\text{CN}$  give smaller than expected photovoltages. Further, the  $E_B$  on the second scan is the same as that found for the oxidized n-CdTe from the oxidizing etch. The point is that  $E_B$  is very sensitive to the extent to which n-CdTe is oxidized after the reducing etch. Redox couples that have  $E_1$  more positive than  $+0.4$  V vs. SCE clearly suffer from the photoanodic decomposition and are borderline Class V couples. Photoanodic decomposition is even more severe in  $\text{H}_2\text{O}$  than in  $\text{CH}_3\text{CN}$  and couples positive of  $+0.1$  V vs. SCE are Class V.

Figure 6 illustrates the behavior of the  $\text{TMPD}^{+}/0$  system at the reduced n-CdTe in  $\text{H}_2\text{O}/0.1 \text{ M NaClO}_4$  solution. This redox couple gives the largest observed value of  $E_B$ ,  $-0.9$  V. This large value of  $E_B$  compared

to that for the oxidized n-CdTe and the establishment of redox couples that give zero and near-zero values of  $E_B$  establish a clear difference between the oxidized and reduced n-CdTe prepared via the etching procedures. For either surface it appears that the  $E_B$  vs.  $E_3$  is independent of whether the solvent is  $\text{CH}_3\text{CN}$  or  $\text{H}_2\text{O}$ . However, in  $\text{H}_2\text{O}$  the potential onset for photoanodic decomposition current is more negative than in  $\text{CH}_3\text{CN}$ , consistent with previous findings for CdS and other photoanode materials.<sup>22</sup>

b. Cyclic Voltammetry of n-CdTe in the Absence of Redox Couples. The n-CdTe electrodes exhibit current-potential properties that are consistent with an important influence from a redox labile CdTe surface in the  $E_B$  determinations. Figure 7 shows the cathodic current in  $\text{H}_2\text{O}/0.1 \text{ M NaClO}_4$  for n-CdTe electrodes pretreated in various ways. As illustrated, an oxidized n-CdTe from the oxidizing etch exhibits a large cathodic current in a potential region where the reduced n-CdTe exhibits none. For all five oxidizing etchants we find dark cathodic currents where the reducing etchant gives none or little. However, a reduced n-CdTe electrode that has been photoanodized in one positive scan does exhibit a large cathodic current. These data illustrate that the oxidized surfaces do behave in a manner that is different compared to the reduced surfaces. However, the nature of the reducible surface species is not clear. It is attractive to conclude that the reduction current is attributable to processes such as that represented by equation (5), since



it appears that oxidation of  $\text{Te}^{2-}$  is the process that occurs in photoanodic decomposition, equation (3).

The reduction according to equation (4) appears to occur at  $\sim -1.6 \text{ V}$  vs. SCE, Figure 7. The reduced n-CdTe exhibits a large cathodic current at sufficiently negative potentials and a return sweep shows surface oxidation

presumably corresponding to the oxidation of Cd back to  $\text{Cd}^{2+}$  and/or  $\text{Te}_x^{2-}$  to a higher oxidation state. Similar processes have been observed for  $\text{CdS}$ .<sup>23c,d</sup>

The irreversible oxidation and reduction of the n-CdTe in the potential range where CdTe has been evaluated with respect to  $E_g$  is clearly responsible for the changes in  $E_g$  that occur with successive cyclic voltammetry scans. Unfortunately, it does not appear that it is possible to electrochemically repair damage that results from photoanodic decomposition. Nor does electrochemical reduction of oxidized n-CdTe from the oxidizing etch change the surface to that generated by the reducing etch procedure. Both the surface electrochemistry and the surface redox chemistry involving the etch solutions is complicated and it does not appear that complete characterization is possible by using only electrochemical techniques. In the section below, we describe surface analyses by XPS and Auger that confirm the rough chemical expectations from an oxidizing vs. reducing pretreatment of CdTe.

c. X-Ray Photoelectron Spectra and Auger Analysis of n-CdTe. Figures 8 and 9 show the XPS and Auger spectra for representative samples of reduced and oxidized CdTe. The spectra show qualitative differences for the oxidized and reduced CdTe. From the oxidizing etch it is logical to conclude that the surface is rich in some form of Te. Previous workers have shown that a Te film can be formed on the surface, and Auger and XPS spectra of CdTe surfaces treated with  $\text{HNO}_3/\text{H}_2\text{O}/\text{K}_2\text{Cr}_2\text{O}_7$  solutions are consistent with the formation of a rather thick, Te-rich overlayer.<sup>24-26</sup> As the earlier workers found, we find that the oxidizing etch yields a surface that does not exhibit a significant signal for Cd. A surface that has been reduced exhibits a strong Cd signal in both the Auger and XPS spectra. Other important features of the spectra are given below.

The reducing etch yields a surface that has a number of impurities that would appear to derive from the etch solution: S, Na, and Cl are present in addition to the ubiquitous C and O. The expected signals for the elements Cd and Te are easily detected and appear as important features in Auger and XPS. Sputtering the surface of either the oxidized or reduced CdTe yields a clean spectrum for CdTe which, excepting for selective sputtering, is probably the spectrum of Cd and Te very close to the 1/1 stoichiometry of CdTe. The XPS of the reduced CdTe in the Cd region, Figure 9, show the Cd signals to be at nearly the same binding energy as for the sputtered surface. However, the signals in the Te region provide evidence for at least two types of Te. One of the sets of signals in the Te region is likely due to  $\text{Te}^{2-}$ , matching the binding energy for the sputtered surface. The higher binding energy set of Te peaks is logically due to an oxidized form of Te. In fact, the samples are exposed to air and it is likely that the Te signals are the same as those obtained from air oxidation of a cleaved crystal. Others have assigned the air oxidation product to  $\text{TeO}_2$ <sup>25</sup> and the observation of an O signal is consistent with such a conclusion. But the main point is that both  $\text{Cd}^{2+}$  and  $\text{Te}^{2-}$  are easily detectable from the reducing etch.

Use of  $\text{Ar}^+$  sputtering can result in surface chemistry to change the oxidation level of the surface species.<sup>27</sup> However, the Cd signals for reduced CdTe are at the same position as for the sputtered sample suggesting that  $\text{Ar}^+$  does not affect the  $\text{Cd}^{2+}$  presumably present. Further, sputtering the reduced surface removes the set of higher binding energy Te signals consistent with the removal of the more oxidized Te material leaving  $\text{Te}^{2-}$ . Thus, we believe that surface damage due to the sputtering technique is relatively unimportant.

The oxidizing etch of CdTe shows impurity signals C, O, and Cr in the electron spectroscopies. The C and O are omnipresent; the Cr logically comes from the use of  $K_2Cr_2O_7$  in the etch solution. The Cr is unequivocally detected in the Auger spectrum, Figure 8; the XPS spectrum is equivocal because the Te and Cr binding energies are very similar. The ~580 eV binding energy region for the oxidized CdTe, Figure 9, is very different than the reduced CdTe. Two, relatively broad signals are observed whose peak positions do not match any of the signals for reduced CdTe. Inasmuch as Cr is detectable in the Auger of the same sample and the Cr XPS signals are about as intense as those for Te,<sup>18</sup> it is likely that some of the intensity in the ~580 eV region is due to some form of Cr. But, since Te is observable in the Auger, some of the intensity is due to some form of Te. Photooxidation of the reduced CdTe or treatment of CdTe with  $Br_2/MeOH$  yields a high ratio of the lower energy to the higher energy Te peaks than the ratio observed for reduced CdTe. Thus, the pair of lower binding peaks are logically a combination of  $Te_x^{2-}$  and  $Te^{2-}$  consistent with the insensitivity of the binding energy to changes in x in  $Te_x^{2-}$ .<sup>18</sup> The higher binding energy Te peaks are likely due to  $TeO_2$ .<sup>25</sup> Interestingly, the oxidizing etch of  $Br_2$  in  $CH_3OH$  does not yield a surface that is as Te-rich as we find for etch (i).<sup>24,25</sup> In fact, the  $Br_2/CH_3OH$  etch appears to yield a Cd/Te element ratio that is close to that for the sputtered surface. The  $Br_2$  must be capable of oxidatively removing elemental Te that is initially formed by the oxidation of the surface such that the  $Te_x^{2-}$  layer is qualitatively thinner than with etch (i). The oxidizing etch used for most of our work produces a very Cd-deficient surface, and we associate the difference in photovoltaic response of reduced and oxidized CdTe with the difference in the amount of  $Te^{2-}$  at the surface.

### Discussion

In electronic device applications and energy conversion applications the surface chemistry of materials can be an important limiting parameter. For CdTe, a material having nearly optimum response to the solar spectrum, photovoltaic devices could give high efficiency. However, the Fermi level pinning yields a relatively low output photovoltage. We have demonstrated that the surface pretreatment associated with the use of several oxidizing etchants results in a Te-rich (Cd-deficient) surface. We associate the Fermi level pinning with the overlayer of Te-rich material. A reducing etch for the CdTe generates a surface that is close to the expected Cd/Te stoichiometry, and in this case the CdTe behaves as a nearly ideal semiconductor with an output photovoltage of up to -0.9 V using the  $\text{TMPD}^{+/0}$  redox couple. The -0.9 V output photovoltage exceeds the photovoltage from the Fermi level pinned system by 0.3 - 0.4 V. However, the removal of Fermi level pinning results in zero photovoltage for redox couples that have  $E_{1/2}$  more negative than -1.0 V vs. SCE, while the Fermi level pinned CdTe gives -0.5 V for such couples.

The demonstration that Fermi level pinning can be manipulated by surface chemistry is an important finding inasmuch as the phenomenon of Fermi level pinning seems to be fairly common for small band gap materials. If the pinning results in a large photovoltage relative to  $E_g$  as in the case of p-InP<sup>28</sup> there may be no advantage in removing pinning, but when the photovoltage is a small fraction of  $E_g$  the pinning is a serious drawback. The removal of Fermi level pinning for n-CdTe does not alter the extreme susceptibility of n-CdTe to photoanodic decomposition at sufficiently positive potentials. However, our results suggest that examination of the Schottky barrier, n-CdTe/metal, behavior using the reducing etch to pretreat the CdTe would be worthwhile. It may be possible to prepare durable

n-CdTe/metal interfaces that give good photovoltages. Previously, it was determined that a photovoltage of 0.68 V could be obtained for Schottky barriers using CdTe;<sup>4a</sup> our data suggest that the reducing etch pretreatment could improve this value.

If we take the Te-rich overlayer on oxidized CdTe to be a layer of elemental Te we can understand the Fermi level pinning of the CdTe to be due to the contact of the underlying CdTe by the Te layer. Support for the conclusion that the overlayer is in fact elemental Te comes from the original literature concerning the oxidizing etch.<sup>12b</sup> Elemental Te is known to have significant conductivity and can be regarded as semimetallic.<sup>29</sup> Contacting the outer Te layer with either metals or a liquid electrolyte will not alter the CdTe/Te interface energetics.<sup>5</sup> Thus, the photovoltage is fixed to the value associated with the CdTe coated by a relatively thick Te overlayer. We should emphasize that this may not be the only mechanism for Fermi level pinning of CdTe. For example, the CdTe/metal barrier height changes by only ~0.2 V for a 1.5 V change in  $\phi$  for the contacting metal<sup>4</sup> where CdTe is pretreated with the  $\text{Br}_2/\text{CH}_3\text{OH}$  etch that yields a near stoichiometric Cd/Te surface.<sup>24-26</sup> The pinning in this instance may be due to interface states associated with a much thinner layer of Te on the surface. If a sufficient density of interface states results from reaction with a metal contact the prospects are not good for improving photovoltage for the CdTe/metal system by using a reducing pretreatment for CdTe. In this connection it is noteworthy that two earlier studies<sup>3</sup> of n-CdTe/liquid interfaces report the use of the  $\text{Br}_2/\text{CH}_3\text{OH}$  pretreatment and claim some results that parallel our findings for the reducing etch. However, photovoltages were not as high as those obtained here and greater difficulty with reproducibility was apparently encountered. It may be that the most efficient devices would then be those based on liquid electrolyte contacts, but the lack of durability remains a major hurdle to the achievement of any useful photoelectrochemical device from exploitation of a reducing etch procedure for n-CdTe. The results, though, do establish that a reproducible surface pretreatment can yield reproducible photovoltage

measurements. Further, the finding that Fermi level pinning can be removed establishes that the extent of ionic vs. covalent bonding in the series CdS, CdSe, and CdTe does not control the value of  $E_g$  or its dependence on  $\phi$  or  $E_{\text{redox}}$ .<sup>4b</sup> Rather, the presence of a layer of semimetallic Te on CdTe can rationalize the earlier observation<sup>2</sup> of a constant  $E_g$  vs.  $E_{\text{redox}}$  for n-CdTe. This work thus establishes one mechanism for Fermi level pinning. Preserving the integrity of the reduced CdTe surface is now the object of our future studies using n-CdTe photoanodes.

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Table 1. Barrier height determinations for oxidized monolayers. Cyclic voltammetry for various Redox Couples in CH<sub>3</sub>CN or H<sub>2</sub>O.<sup>a</sup>

| Redox Couple (Class), <sup>b</sup>   | E <sub>1</sub> | Solvent            | E <sub>PA,Pt</sub> | E <sub>PA,n-CdTe,illum.</sub> | E <sub>V</sub> , V (+100 mV) |
|--|----------------|--------------------|--------------------|-------------------------------|------------------------------|
| TMPD <sup>2+/+</sup> (IV), 1   | +0.70          | CH <sub>3</sub> CN | +0.72              | +0.13                         | 0.59                         |
| TMPD <sup>+0</sup> (IV), 2   | +0.10          | CH <sub>3</sub> CN | +0.14              | -0.45                         | 0.59                         |
| Fe( <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> <sup>+0</sup> (IV), 3 | +0.40          | CH <sub>3</sub> CN | +0.43              | -0.19                         | 0.62                         |
| Fe( <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> <sup>+0</sup> (IV), 4 | -0.12          | CH <sub>3</sub> CN | -0.07              | -0.62                         | 0.55                         |
| MV <sup>2+/+</sup> (IV), 5   | -0.45          | CH <sub>3</sub> CN | -0.41              | -0.93                         | 0.52                         |
| MV <sup>+0</sup> (IV), 6   | -0.85          | CH <sub>3</sub> CN | -0.82              | -1.32                         | 0.50                         |
| Ru(bpy) <sub>3</sub> <sup>2+/+</sup> (IV), 7   | -1.34          | CH <sub>3</sub> CN | -1.29              | -1.77                         | 0.48                         |
| Ru(bpy) <sub>3</sub> <sup>+0</sup> (IV), 8   | -1.49          | CH <sub>3</sub> CN | -1.48              | -1.99                         | 0.51                         |
| Ru(bpy) <sub>3</sub> <sup>0/-</sup> (IV), 9  | -1.73          | CH <sub>3</sub> CN | -1.71              | -2.32                         | 0.61                         |
| Anthracene <sup>0/-</sup> (IV)   | -1.99          | CH <sub>3</sub> CN | -1.95              | -2.24                         | 0.29                         |
| Fe(CN) <sub>6</sub> <sup>3-/4-</sup> (IV), 1   | +0.21          | H <sub>2</sub> O   | +0.30              | -0.31                         | 0.61                         |
| TMPD <sup>+0</sup> (IV), 2   | +0.02          | H <sub>2</sub> O   | +0.06              | -0.43                         | 0.49                         |
| Ru(NH <sub>3</sub> ) <sub>6</sub> <sup>3+/2+</sup> (IV), 3                           | -0.19          | H <sub>2</sub> O   | -0.12              | -0.64                         | 0.52                         |
| AQ <sup>0/2-</sup> (IV), 4   | -0.56          | H <sub>2</sub> O   | -0.40 <sup>c</sup> | -0.93                         | 0.53                         |
| MV <sup>2+/+</sup> (IV), 5   | -0.61          | H <sub>2</sub> O   | -0.54 <sup>c</sup> | -1.07                         | 0.53                         |
| TQ <sup>2+/+</sup> (IV), 6   | -0.81          | H <sub>2</sub> O   | -0.77 <sup>c</sup> | -1.15                         | 0.38                         |

<sup>a</sup> Conditions for etching and cyclic voltammetry are given in the Experimental unless otherwise noted.

Data for CH<sub>3</sub>CN are from ref. 2. All potentials, E<sub>1</sub>, E<sub>PA,Pt</sub>, E<sub>PA,n-CdTe,illum.</sub>, are given in volts vs. SCE.

<sup>b</sup> = refers to data points on plots in Figure 1. For Class definitions see text.

<sup>c</sup> Measured at Hg working electrode.

Table II. Barrier Height Determinations for Reduced n-CdTe by Cyclic Voltammetry for Various Redox Couples in CH<sub>3</sub>CN or H<sub>2</sub>O.<sup>a</sup>

| Redox Couple (Class), <sup>b</sup>   | E <sub>1/2</sub> | Solvent            | E <sub>PA,pt</sub> | E <sub>PA,n-CdTe,illum.</sub> | E <sub>g</sub> , V (+100 mV) |
|--|------------------|--------------------|--------------------|-------------------------------|------------------------------|
| TMPD <sup>2+/+</sup> (III,V), 1  | +0.70            | CH <sub>3</sub> CN | +0.79              | +0.22                         | 0.57                         |
| Fe(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> <sup>+0</sup> (III,V), 2 | +0.40            | CH <sub>3</sub> CN | +0.48              | -0.26                         | 0.74                         |
| TMPD <sup>+0</sup> (III), 3  | +0.10            | CH <sub>3</sub> CN | +0.19              | -0.53                         | 0.72                         |
| Fe(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> <sup>+0</sup> (III), 4  | -0.12            | CH <sub>3</sub> CN | -0.07              | -0.69                         | 0.62                         |
| TQ <sup>2+/+</sup> (III), 5  | -0.59            | CH <sub>3</sub> CN | -0.52              | -0.76                         | 0.24                         |
| TQ <sup>+0</sup> (III), 6  | -0.89            | CH <sub>3</sub> CN | -0.82              | -1.00                         | 0.18                         |
| Ru(bipy) <sub>3</sub> <sup>2+/+</sup> (I)  | -1.34            | CH <sub>3</sub> CN | -1.29              | -1.29 (dark or light)         | 0.00                         |
| Ru(bipy) <sub>3</sub> <sup>+0</sup> (I)  | -1.49            | CH <sub>3</sub> CN | -1.48              | -1.48 (dark or light)         | 0.00                         |
| TMPD <sup>+0</sup> (III), 1  | +0.02            | H <sub>2</sub> O   | +0.07              | -0.79                         | 0.86                         |
| Ru(NH <sub>3</sub> ) <sub>6</sub> <sup>3+/2+</sup> (III), 2                              | -0.19            | H <sub>2</sub> O   | -0.14              | -0.70                         | 0.56                         |
| Eu <sup>3+/2+</sup> (III), 3   | -0.64            | H <sub>2</sub> O   | -0.54              | -1.07                         | 0.48                         |
| TQ <sup>2+/+</sup> (III), 4  | -0.81            | H <sub>2</sub> O   | -0.77 <sup>c</sup> | -1.03                         | 0.26                         |

<sup>a</sup> Conditions as in Table I and Experimental.

<sup>b</sup> # refers to data entries on plots in Figure 1. For Class definition see text

<sup>c</sup> Measured at Hg working electrode.

### Figure Captions

Figure 1. Plots of photovoltage for n-CdTe treated with either the reducing or oxidizing etch as a function of the  $E_{\text{redox}}$  of the solution. Data are determined by cyclic voltammetry as described in the text and in the Experimental. The numbers for the individual data points are keyed to the redox couples in Tables I and II.

Figure 2. Representative data for cyclic voltammetry of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple at a Pt electrode and an oxidized n-CdTe electrode.

Figure 3. Cyclic voltammetry for the  $\text{TQ}^{2+/\cdot+}$  and for the  $\text{TQ}^{\cdot+}/0$  couples at Pt and at reduced n-CdTe.

Figure 4. Cyclic voltammetry on the left compares the response of  $\text{Fe}(\cdot^5\text{-C}_5\text{H}_5)_2^{+/0}$  at Pt and reduced n-CdTe. The data on the right illustrate the consequences of photoanodic decomposition of n-CdTe by a positive excursion beyond the photoanodic current peak for the  $\text{Fe}(\cdot^5\text{-C}_5\text{H}_5)_2^{+/0}$  couple. Scan 1 is the first scan and scan 2 is the second scan under the same conditions as the data on the left for n-CdTe.

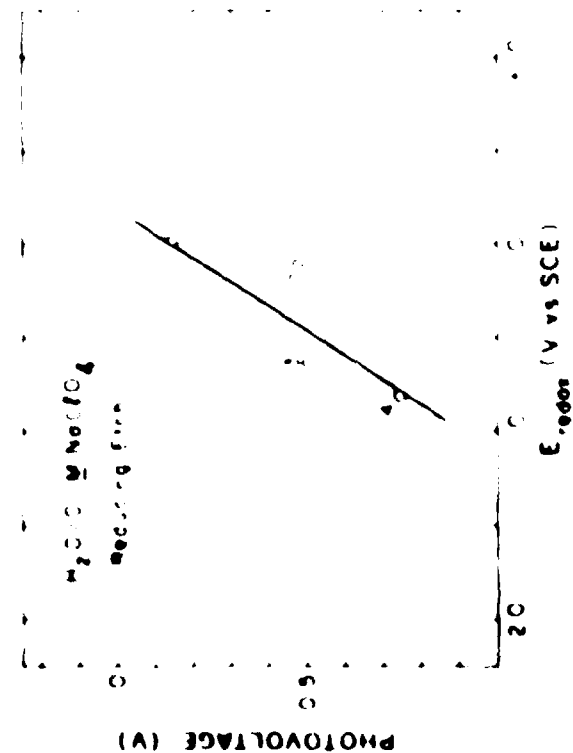
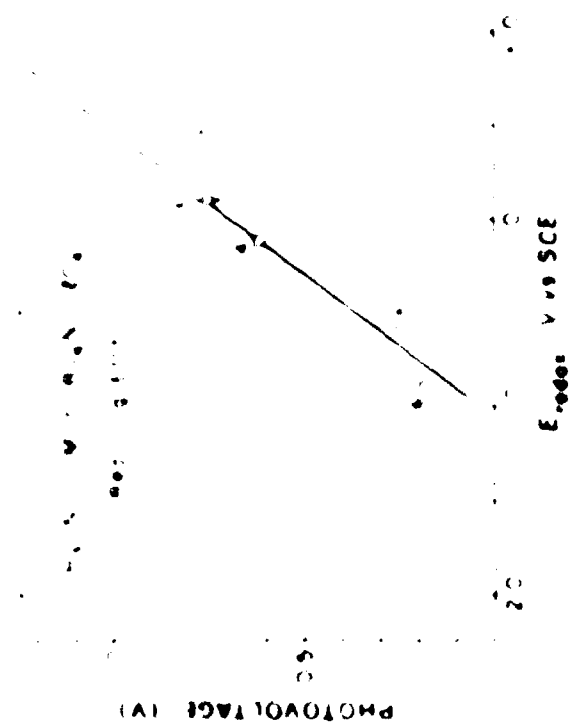
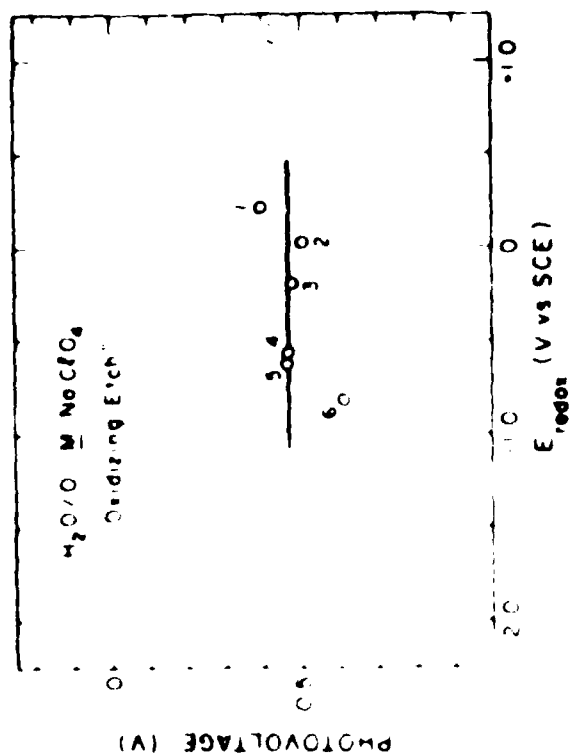
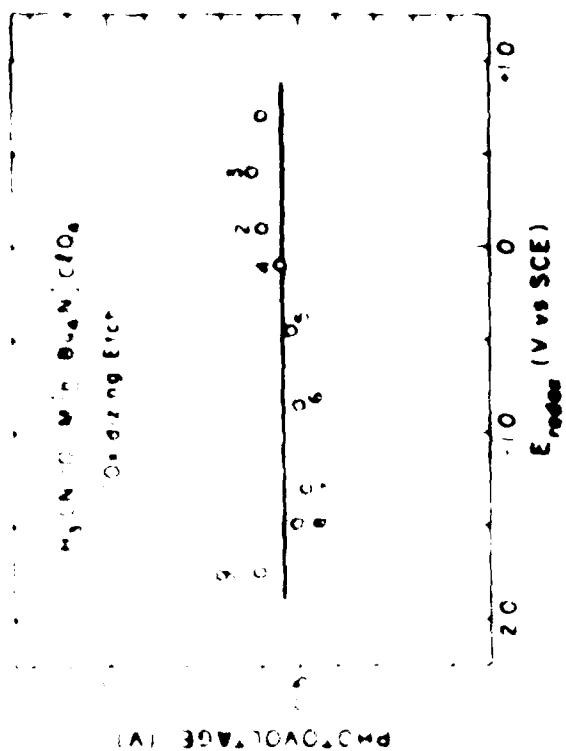
Figure 5. Cyclic voltammetry for  $\text{TMPD}^{2+/\cdot+}$  (positive peak) and  $\text{TMPD}^{\cdot+}/0$  (negative peak) at illuminated (reduced) n-CdTe on the first scan, 1 (—), and second scan, 2 (----), from an initial potential of -1.0 V vs. SCE.

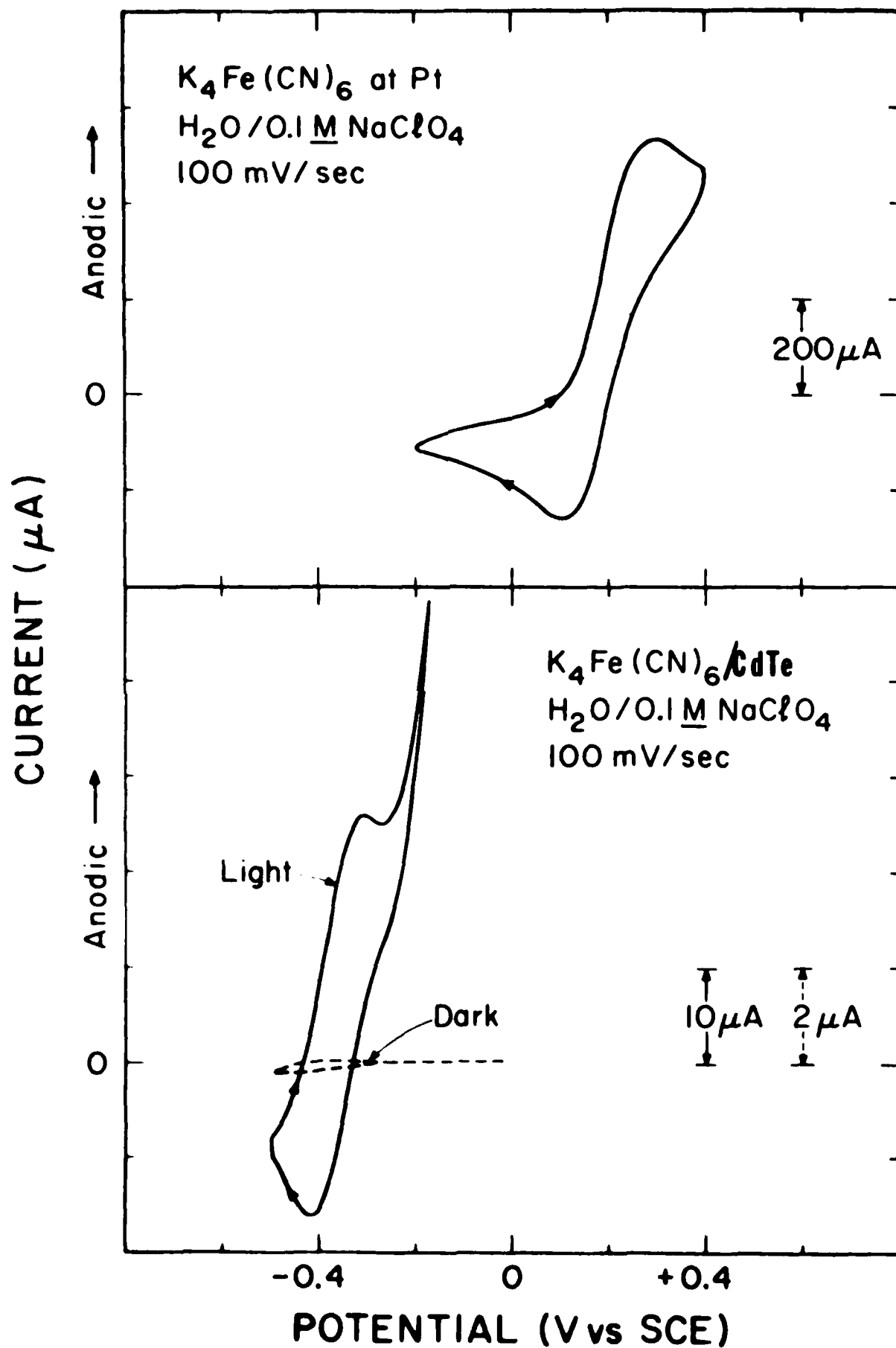
Figure 6. Comparison of cyclic voltammetry for TMPD at Pt and reduced n-CdTe showing almost 0.9 V more negative  $\text{TMPD} \rightarrow \text{TMPD}^{\cdot+}$  peak at illuminated n-CdTe compared to Pt. The dashed curve for n-CdTe is the dark response.

Figure 7. (Left) Dark cathodic current of n-CdTe in  $\text{H}_2\text{O}/0.1 \text{ M NaClO}_4$  at 5 mV/s. (a) n-CdTe etched with etchant (i) in the experimental, (b) n-CdTe etched with the reducing etch; (c) reduced n-CdTe scanned once from -1.4 to +0.35 V vs. SCE at 100 mV/s under illumination ( $50 \text{ mW/cm}^2$ ) in  $\text{CH}_3\text{CN}/0.1 \text{ M [n-Bu}_4\text{N]ClO}_4$  to oxidize the surface. In each case the initial potential is 0.0 V vs. SCE. (Right) Dark current-voltage curve of n-CdTe etched with the reducing etch in  $\text{H}_2\text{O}/0.1 \text{ M NaClO}_4$  at 5 mV/s. The cathodic limit for (a) (—) is -1.9 V vs. SCE and significant oxidation current results on the return sweep. A freshly reduced electrode scanned to -1.4 V vs. SCE, (b) (---), shows neither significant oxidation nor reduction current. The initial potential in both cases is 0.0 V vs. SCE.

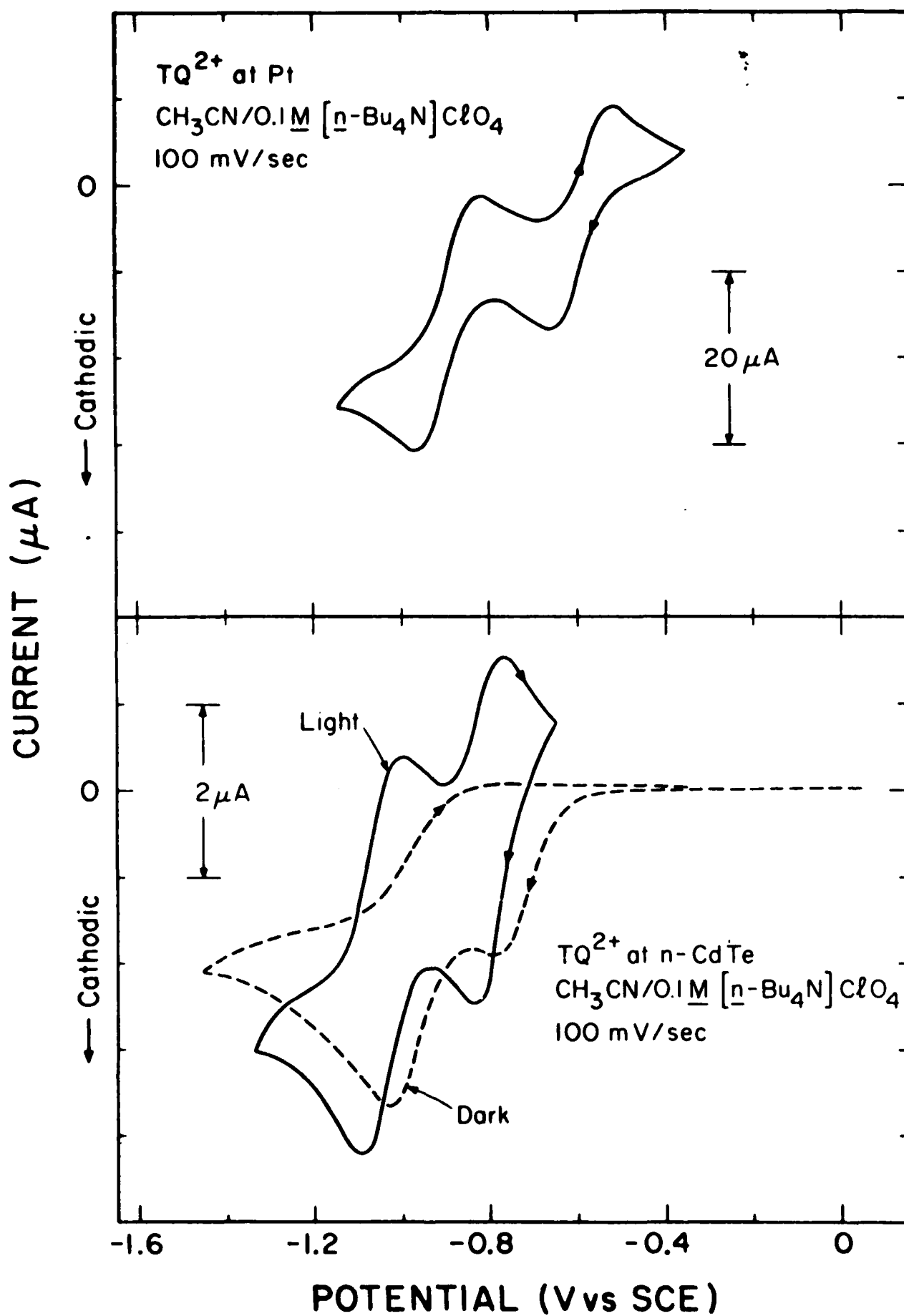
Figure 8. Left three spectra are XPS spectra (scale = 1000 counts/div) and the right three spectra are Auger spectra. The top spectra are for n-CdTe etched using reducing etch; the middle spectra are for n-CdTe etched with the oxidizing etch (i), and the bottom spectra are for n-CdTe sputtered with  $\text{Ar}^+$  until no changes in the Cd/Te signal ratios are observed. The sensitivity for the Auger spectrum of the sputtered sample is 10 times that of the other two.

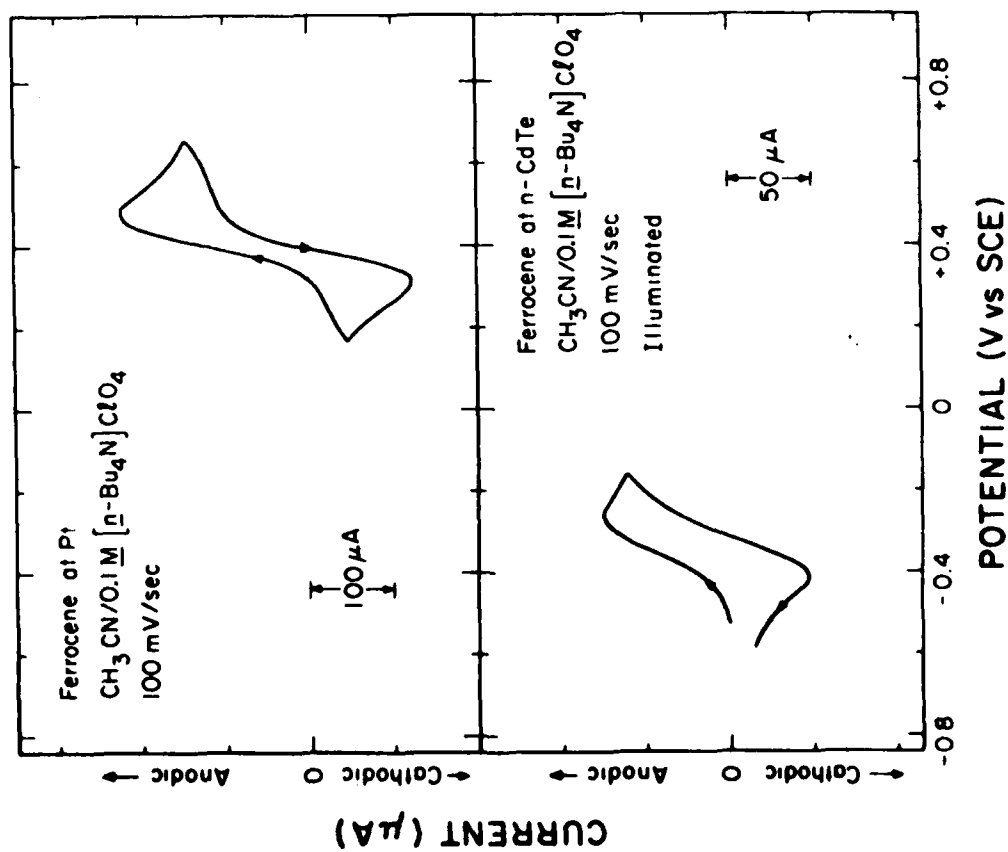
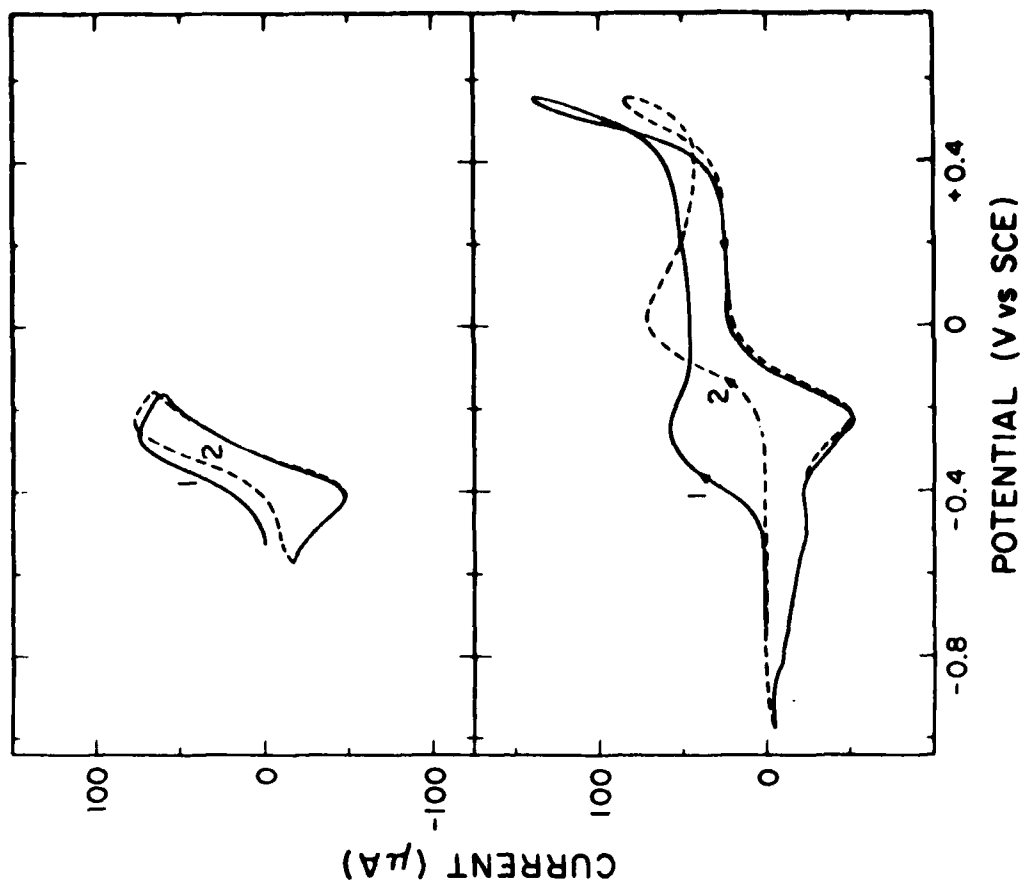
Figure 9. XPS spectra of Te,  $3d_{3/2}$  and  $3d_{5/2}$  signals for (a) n-CdTe etched with the oxidizing etch (i) (scale = 1000 counts/div); (b) n-CdTe etched using reducing etch (scale = 300 counts/div); (c) n-CdTe etched using oxidizing etchant (scale = 300 counts/div). XPS spectra of (d,  $3d_{3/2}$  and  $3d_{5/2}$  signals) for (d)  $\text{Ar}^+$  sputtered n-CdTe (scale = 1000 counts/div) and (e) n-CdTe etched using the reducing etch (scale = 300 counts/div). The samples for (b), (c) and (e) are the same used for the spectra shown in Figure 8.

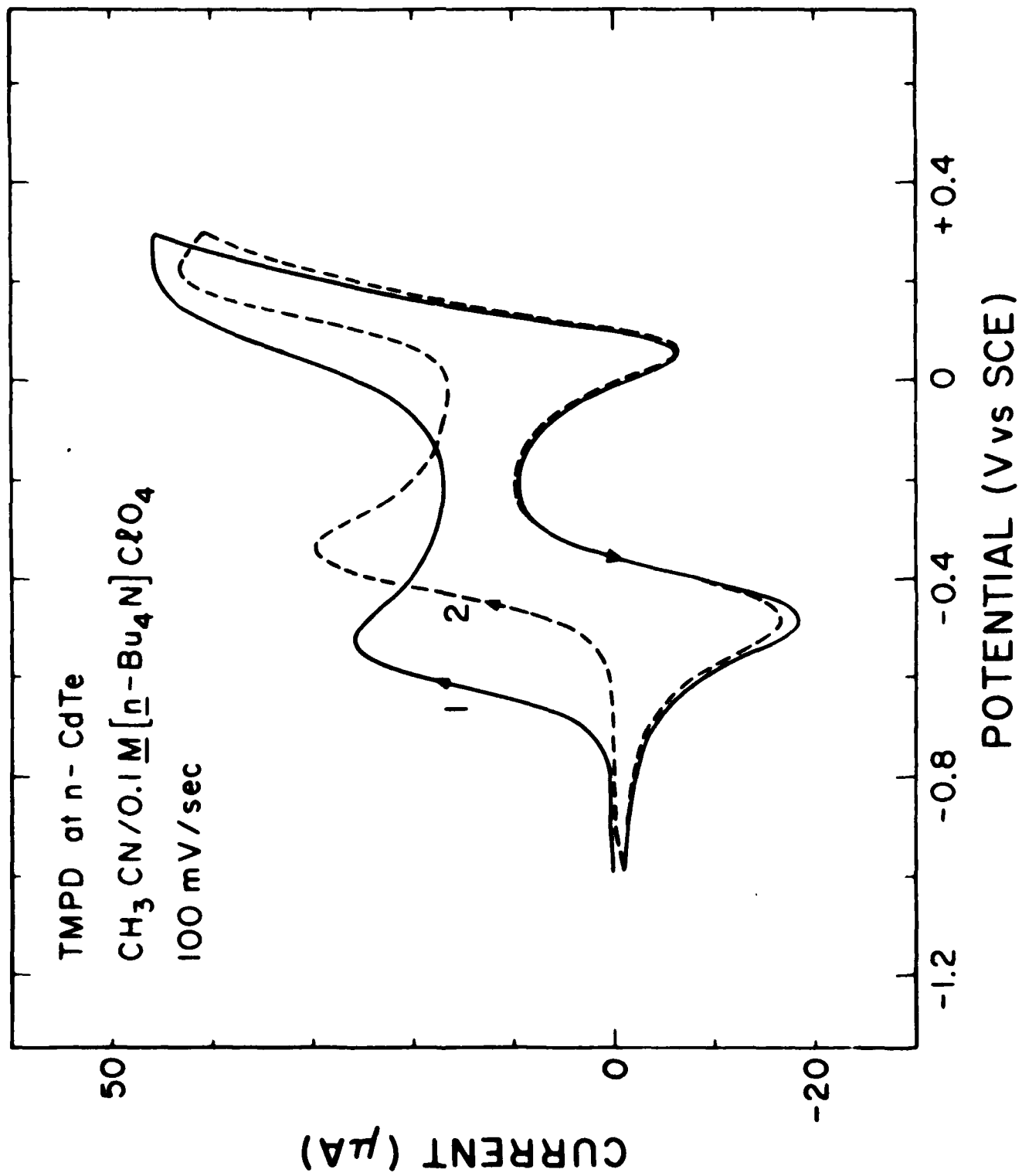


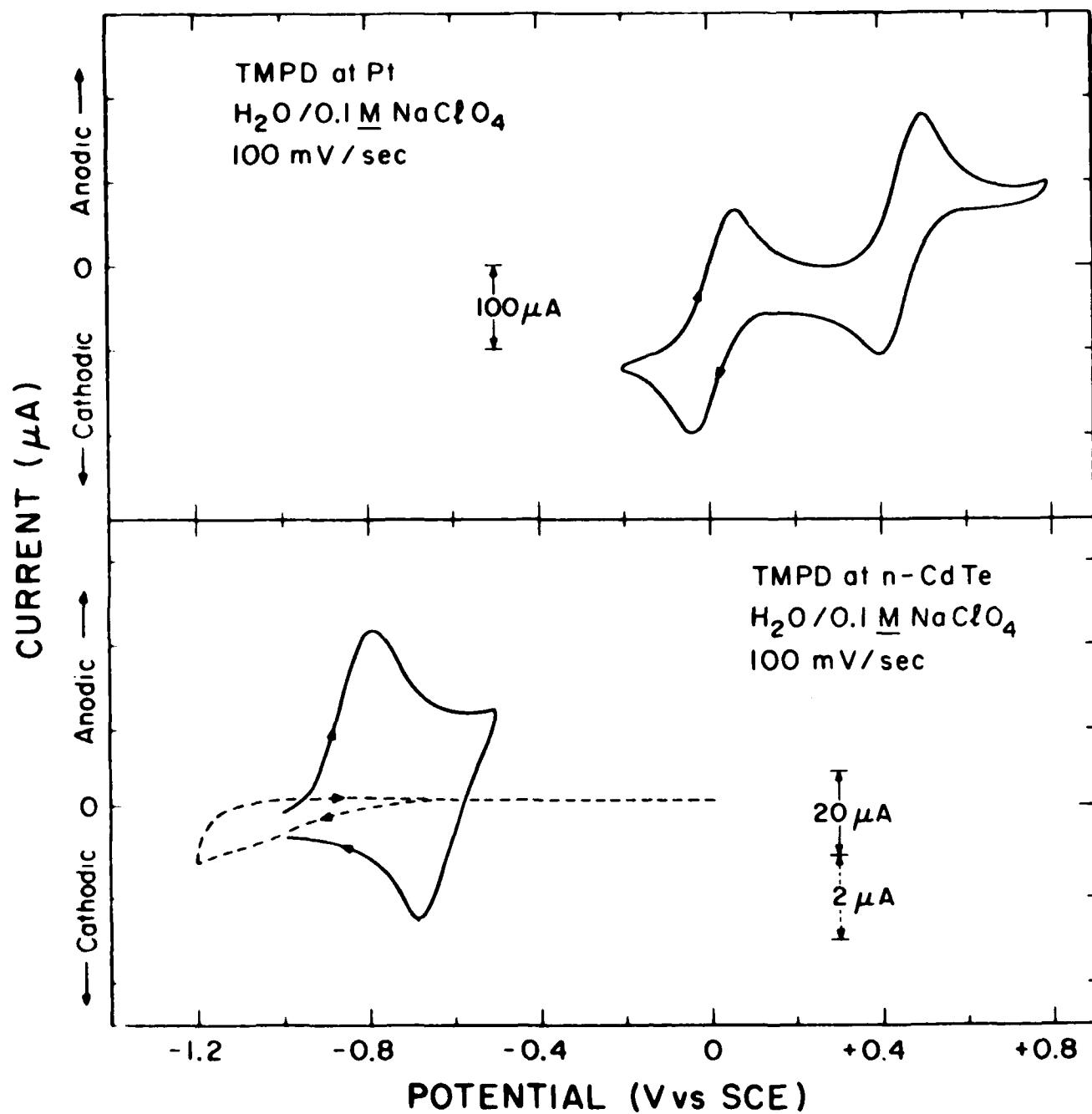


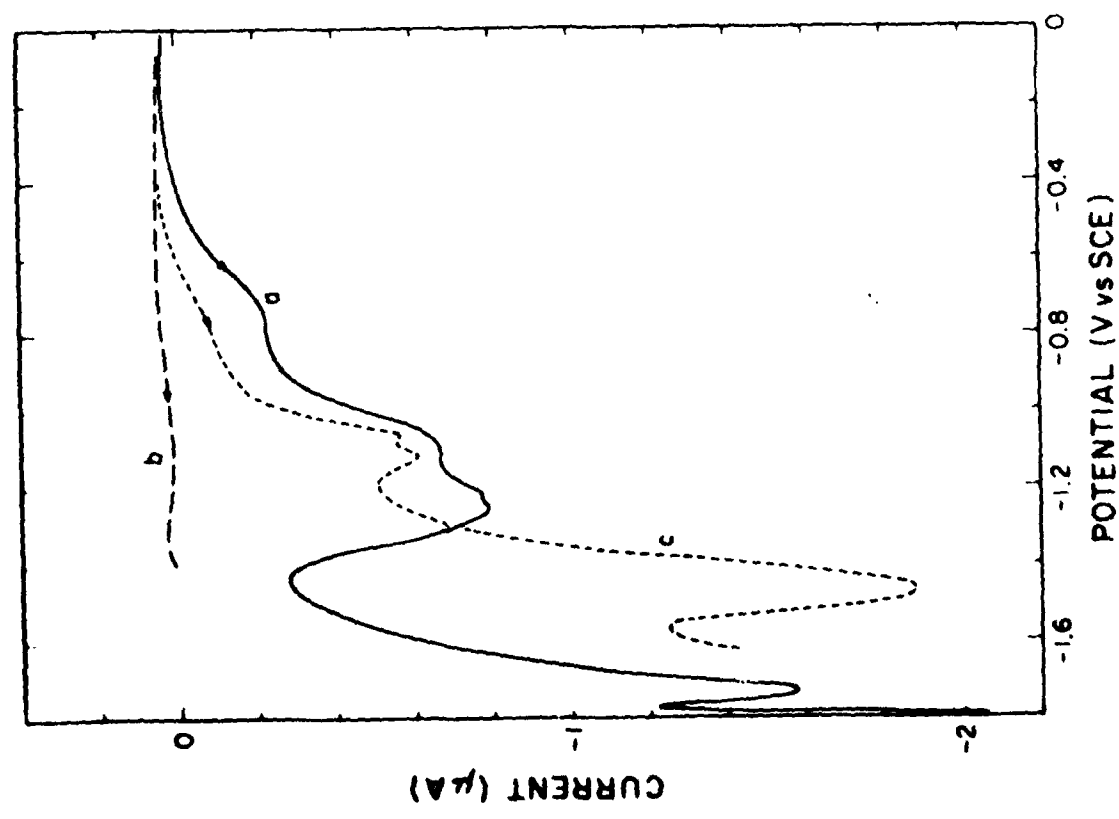
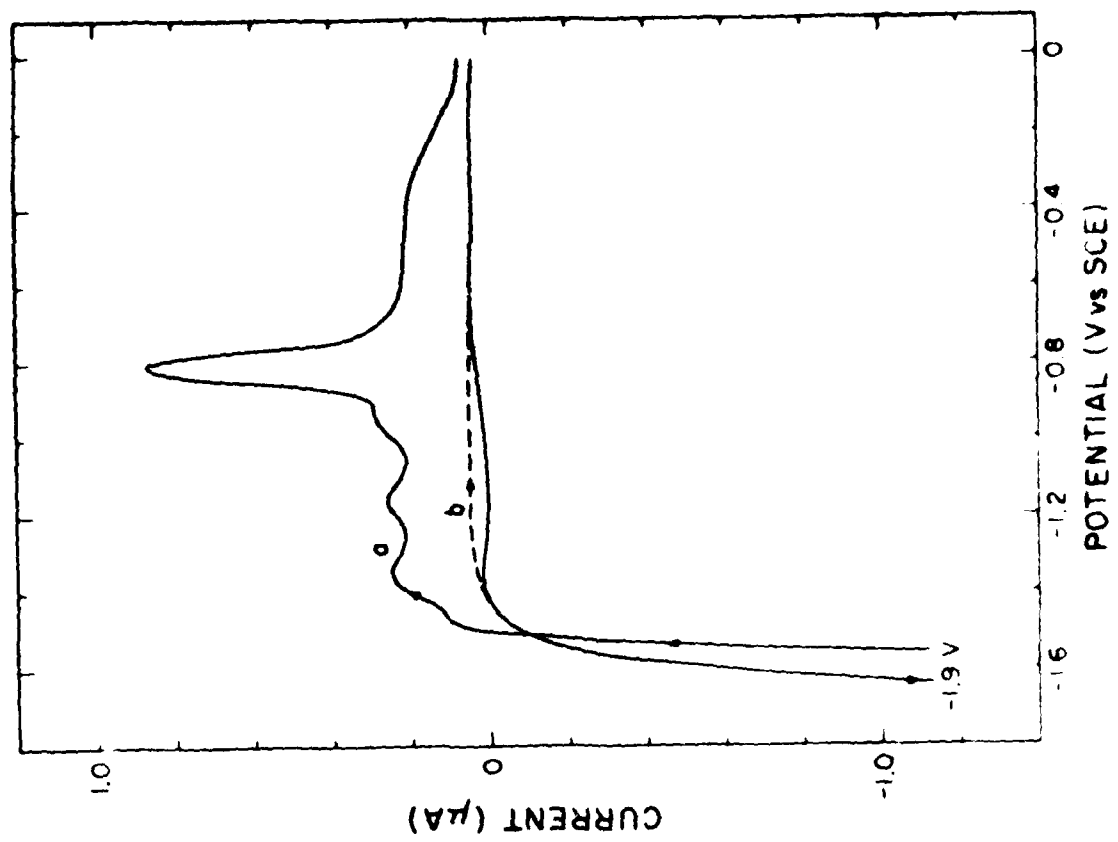


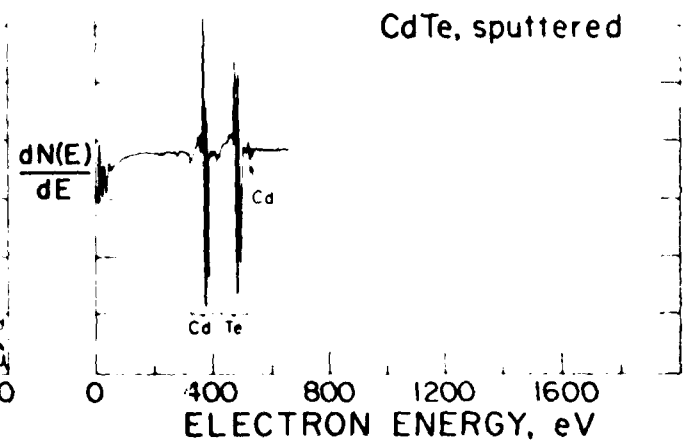
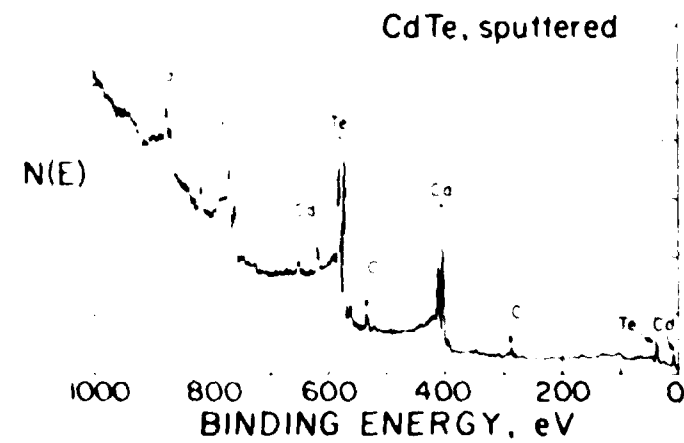
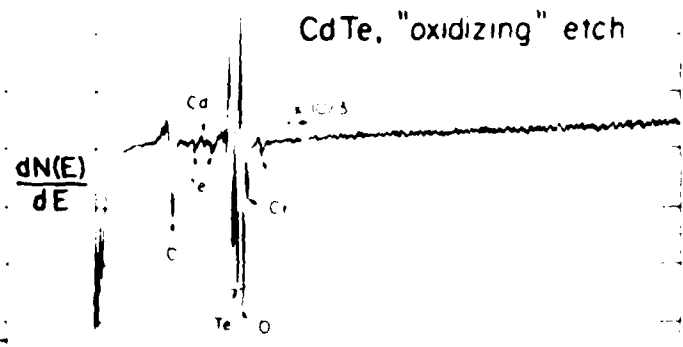
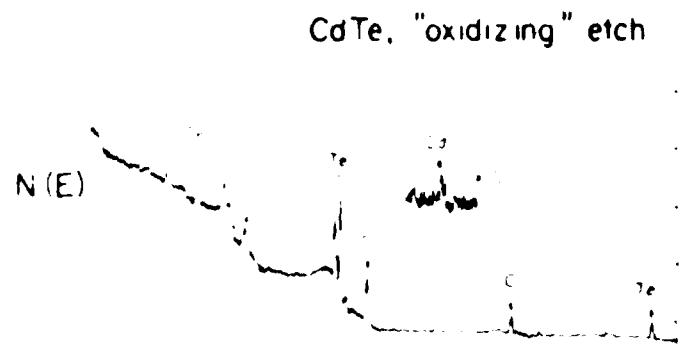
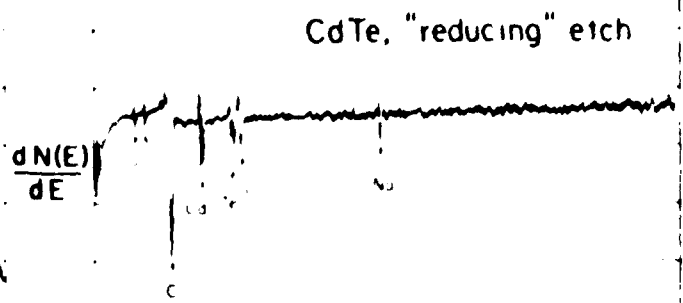
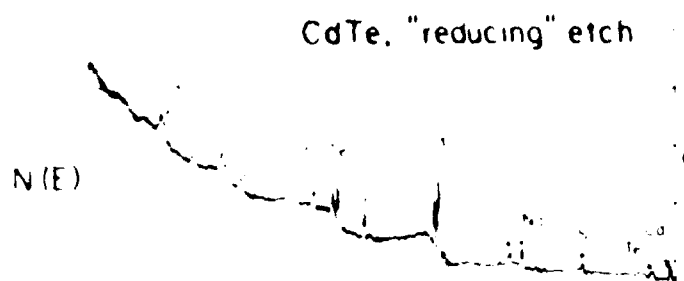


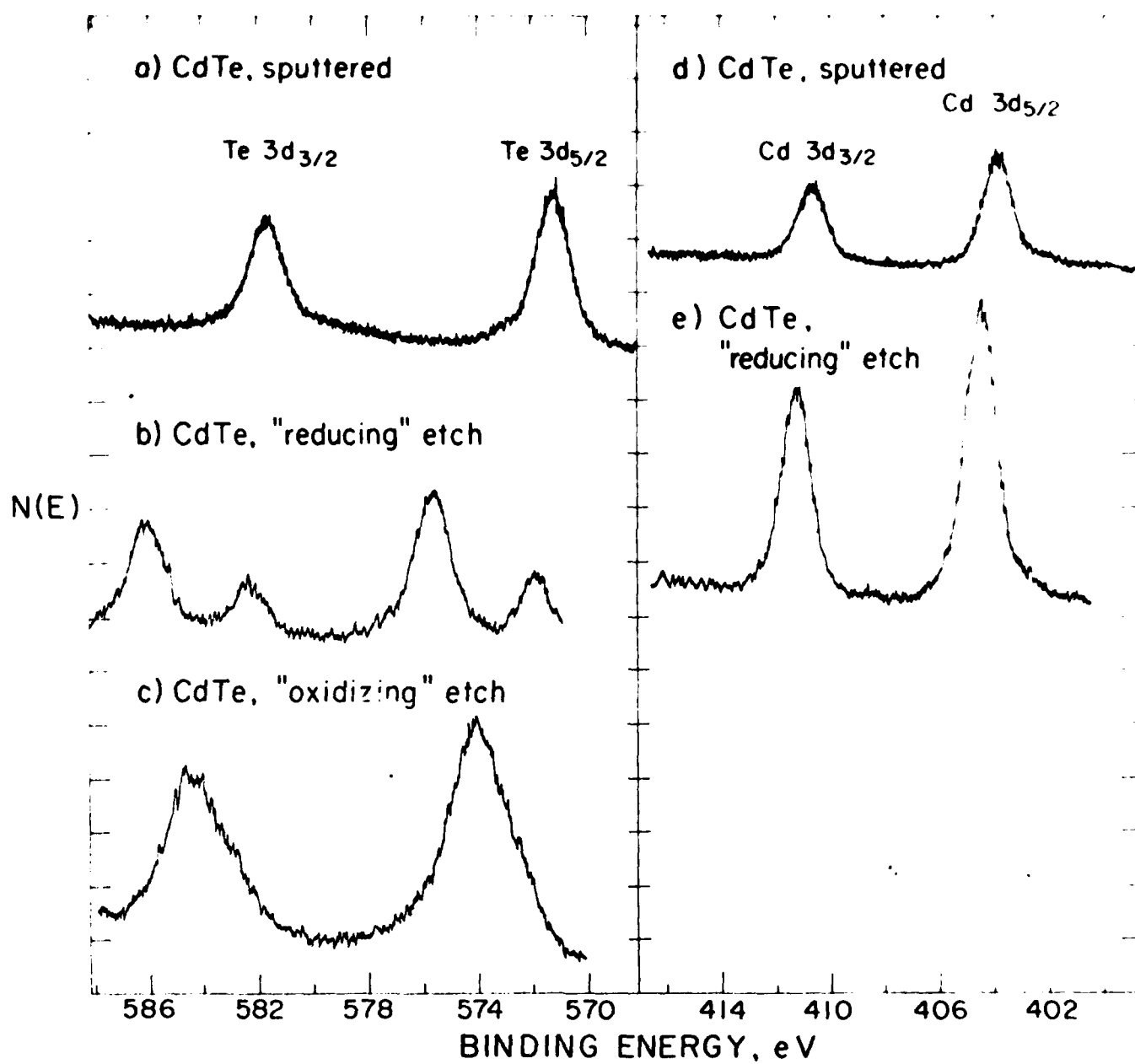












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1. The first step is to identify the problem or question that needs to be answered. This involves understanding the context and the specific requirements of the task.

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